Contribution of dehydration and depolymerization reactions during the fast pyrolysis of various salt-loaded celluloses at low temperatures

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HIGHLIGHTS

- Mg/Ca are more effective than Na/K in catalyzing cellulose dehydration during heating-up.
- Most of Mg/Ca (but little Na/K) become water insoluble during cellulose heating-up.
- Cellulose dehydration is significantly catalyzed by Na/K but not Mg/Ca during isothermal pyrolysis.
- Depolymerization is trivial during cellulose heating-up but important during isothermal pyrolysis.

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ABSTRACT

The loaded salts (NaCl, KCl, MgCl$_2$, and CaCl$_2$) have significantly different influence on the contribution of dehydration and depolymerization reactions to the decomposition of sugar structures during cellulose fast pyrolysis at 325 °C. The structures of salt-loaded celluloses already become cross-linked during heating-up period, largely due to the enhanced dehydration reactions catalyzed by inorganic species. As stronger Lewis acids, the alkaline earth metal ions (Mg^{2+} and Ca^{2+}) are more effective than the alkali metal ions (Na$^+$ and K$^+$) to catalyze the dehydration reactions of sugar structures, leading to the formation of more cross-linked cellulose for the alkaline earth metal chloride-loaded celluloses. As a result, the majority of Mg and Ca are transformed into water-insoluble forms during the heating-up period, largely reducing the catalytic effects of these species on the dehydration of sugar structures during the subsequent isothermal pyrolysis. Rather, the dehydration of non-sugar structures is enhanced because the catalytic species are already bonded with non-sugar structures. In contrast, the dehydration of sugar structures during the heating-up period is less significant for the NaCl-loaded and KCl-loaded celluloses. The majority of Na and K are water-soluble after the heating-up period so that the dehydration of sugar structures is further enhanced during isothermal pyrolysis. The loaded salts have less influence on the depolymerization reactions. The contribution of depolymerization reactions to sugar conversion is relatively small during the heating-up stage, but increases substantially during isothermal pyrolysis.

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1. Introduction

Biomass is considered to be an important source for biofuels production, especially via the technical route of bio-oil production from fast pyrolysis followed by biorefinery [1,2]. However, bio-oil as a feedstock suffers from several key undesired features including high acidity [2,3], low heating value [3] and high viscosity [1,4,5]. Therefore, fundamental understanding on biomass

pyrolysis chemistry and mechanisms is essential to realizing the production of high-quality bio-oil.

Lignocellulosic biomass has complex macromolecular structures which consist of three major oxygen-containing organic polymers including cellulose, hemicellulose, and lignin [6]. The pyrolysis of biomass and its model compounds (cellulose, hemicellulose and lignin) experiences complex chemical reactions during pyrolysis [7–10]. The formation of a liquid intermediate during the pyrolysis of biomass or its model compounds (such as cellulose) is an important phenomenon which has not been clearly understood yet [11–13]. Such a liquid intermediate as the precursors of volatiles strongly determines the properties of produced

bio-oil. Biomass also contains abundant inherent inorganic species (e.g., alkali and alkaline metallic species) which can have significant effects on biomass pyrolysis and bio-oil production [14]. Our recent study [15] revealed the fundamental mechanism of the $MgCl_2$ loading in weakening the hydrogen bonding network within the macromolecular structures of cellulose during pyrolysis. Significant dehydration reactions take place even during the heating-up period, leading to the formation of a highly cross-linked cellulose during the subsequent pyrolysis. The nature of salts added into cellulose is widely known to be a critical factor that alters the reaction mechanism and the properties of pyrolysis products [16–20]. Unfortunately, no study has been carried out to investigate the effect of different alkali and alkaline earth metal species on the contribution of dehydration and depolymerization reactions during the fast pyrolysis of salt-loaded celluloses.

Therefore, this paper continues the work reported in our recent study [15] and aims to understand the significantly different contribution of dehydration and depolymerization reactions during the fast pyrolysis of cellulose samples loaded with various alkali and alkaline earth metal chlorides including NaCl, KCl, $MgCl_2$ and $CaCl_2$.

2. Experiments

2.1. Materials and fast pyrolysis experiments

Cellulose was purchased from a commercial supplier (Sigma–Aldrich, Avicel PH-101) and sieved to a size fraction of 75–106 μm. The size-fractioned cellulose sample was then washed by deionized water to remove water-soluble components that may exist originally. This washed cellulose is hereafter referred to as "raw" cellulose. A set of salt-loaded cellulose samples were prepared from the raw cellulose via wet impregnation using a suitable amount of each salt (NaCl, KCl, $MgCl_2$ or $CaCl_2$) at ~0.025 mol salt per mole of glucose unit. A drop-tube/fixed-bed quartz reactor (carrier gas: Argon), described elsewhere [21,22], was used for the conduction of fast pyrolysis experiments of the raw and salt-loaded cellulose samples. In each experiment, the pyrolysis reactor was firstly preheated to 325 °C. Approximately 0.3 g of sample was then fed into the reactor in one shot, followed by holding the reactor at the temperature for various holding times. Once the pyrolysis experiment is finished, the reactor was taken out of the furnace and rapidly cooled down to room temperature with argon continuously flowing through the reactor. For the pyrolysis experiment at zero holding time, the reactor was taken out of the furnace immediately after the sample bed temperature reached 325 °C, as monitored by a thermocouple. The initial heating rate is estimated to be ~150 °C s^{-1}, according to a method detailed elsewhere [23]. The solid residue after pyrolysis was then collected and the weight loss of the sample during pyrolysis was also determined.

2.2. Sample characterization and analysis

In this study, the solid residue was separated into water-soluble and water-insoluble portions, which are referred as to water-soluble and water-insoluble intermediates, respectively. As raw cellulose is insoluble in water, the water-soluble compounds in the pyrolyzed solid residue are indeed produced from pyrolysis reactions. The water-soluble portion were obtained via the extraction of the solid residues using deionized water at room temperature according to a procedure detailed elsewhere [24,25]. The concentration of the total organic carbon in the solution after extraction was quantified using a Shimadzu total organic carbon (TOC) analyzer. The yield of water-soluble intermediates (on a carbon basis) was then normalized as the percentage of the total

carbon in the raw cellulose fed into the reactor. The carbon contents of the solid residues were analyzed by a PerkinElmer elemental analyzer for the determination of cellulose conversion based on carbon. The total sugar contents in the liquid and solid samples were determined, via the post-hydrolysis technique described elsewhere [26], for the determination of cellulose conversion based on sugar. The inorganic species in the solid samples were determined using a method detailed elsewhere [27].

3. Results and discussion

3.1. Differences in conversions during the pyrolysis of various salt-loaded celluloses

Fig. 1 presents the results on the cellulose conversions based on weight, sugar, carbon for the raw and various salt-loaded celluloses during pyrolysis under the experimental conditions. The data for the raw and $MgCl_2$-loaded celluloses are adapted from our recent work [15]. The conversion on a sugar basis is calculated based on the number of mono-sugar units remained in the solid residue (quantified via post-hydrolysis) as a percentage of those in the initial cellulose. The conversion on a carbon basis is calculated based on the carbon remained in the solid residue as a percentage of the total carbon in the raw cellulose. Similar conversions on bases of weight, sugar and carbon would suggest that depolymerization reactions take place to release anhydro-sugars, while a lower carbon conversion indicates that dehydration reactions play an important role during pyrolysis. The data in Fig. 1 suggest that the addition of salts significantly changes the cellulose conversion during pyrolysis at 325 °C. Compared to the raw cellulose, the cellulose weight conversions of various salt-loaded celluloses are initially higher during the heating-up period, but increase slowly during the isothermal pyrolysis and start to level off at middle conversions (i.e., 40–60%), leading to higher char yields. Significant differences in the cellulose conversions can be found during the pyrolysis of various salt-loaded celluloses. The weight conversions of the salt-loaded celluloses generally follow an order of $MgCl_2$-loaded > NaCl-loaded > KCl-loaded > $CaCl_2$-loaded. It seems that although $MgCl_2$ and $CaCl_2$ are both alkali earth metal chlorides, their effects on cellulose weight conversion during pyrolysis are quite different. The weight conversion of the $MgCl_2$-loaded cellulose is much higher than that of the $CaCl_2$-loaded cellulose.

In comparison to weight conversion, a considerable degree of sugar conversion takes place in the heating-up period during the pyrolysis of various salt-loaded celluloses (see Fig. 1b). The data in Fig. 1b further indicate that the addition of alkaline earth metal chlorides has a much stronger effect on the sugar conversion than the addition of alkali metal chlorides. For instance, ~50% and ~42% of sugar structures are decomposed during the heating-up period for the $CaCl_2$-loaded and $MgCl_2$-loaded celluloses, respectively, in comparison to ~22% for the NaCl-loaded cellulose and ~24% for the KCl-loaded cellulose. During the isothermal pyrolysis, although the sugar conversions for salt-loaded celluloses all increase with holding time, some differences still can be observed from various salt-loaded celluloses. For example, in comparison to other salt-loaded celluloses, the sugar conversion for the $CaCl_2$-loaded cellulose increases more slowly during the isothermal pyrolysis.

Compared to a high sugar conversion of ~50% for the $CaCl_2$-loaded cellulose during the heating-up period, its carbon conversion is only ~3%. Obviously, significant dehydration reactions of sugar structures occur during the heating-up period. The depolymerization reactions start to play an important role during the isothermal pyrolysis, as the carbon conversion starts to increase with increasing the holding time. The carbon conversions for various salt-loaded celluloses are all lower than that for raw cellulose.
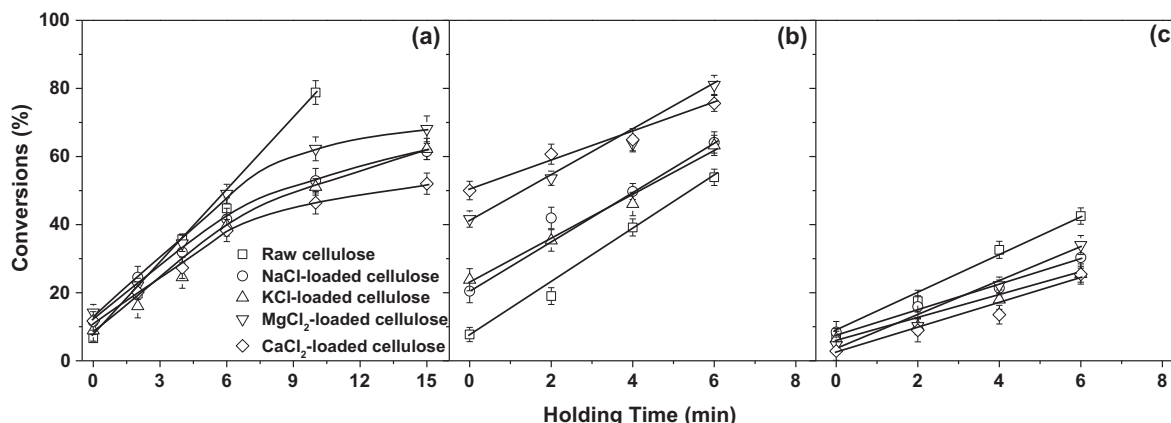
Fig. 1. Cellulose conversions during the pyrolysis of raw and salt-loaded celluloses at 325 °C. Panel (a) weight (on a daf basis); (b) sugar; (c) carbon.

Among the salt-loaded celluloses, the CaCl$_2$-loaded cellulose has the lowest carbon conversion during the isothermal pyrolysis. This indicates that the depolymerization reactions play a less important role for the CaCl$_2$-loaded cellulose during the isothermal pyrolysis, probably due to the significant destruction of sugar structures during the heating-up period.

Elemental analysis of the solid residues was further conducted, and the Van Krevelen diagram is plotted in Fig. 2. It can be found that the sugar conversions during the heating-up period are indeed mainly due to dehydration, as the solid residues after the heating-up period exactly sit in the dehydration lines. The dehydration reactions are more significant for the alkali earth metal chloride-loaded celluloses. Our recent work [15] indicated that the cross-linking reactions are mainly responsible for the dehydration of the MgCl$_2$-loaded cellulose during the heating-up period, due to the weakening of hydrogen bonding networks during the wet impregnation and the heating processes [15,28]. This study

provides further evidences to show that both alkali and alkaline earth metal chlorides promote the dehydration reactions, but the catalytic effects of alkaline earth metal chlorides are much stronger. One important reason is that, compared to alkali metal ions, the alkaline earth metal ions are stronger Lewis acids [29,30]. Therefore, the alkaline earth metal ions have more significant effects to catalyze the dehydration reactions.

3.2. Differences in the solid residues from the pyrolysis of various salt-loaded celluloses

3.2.1. Yield of water-soluble intermediates

To further understand the differences among the salt-loaded celluloses during pyrolysis, the yields of water-soluble intermediates were determined based on carbon in cellulose. Fig. 3 shows the yield of water-soluble intermediates as a function of cellulose weight conversion. The yields of water-soluble intermediates from
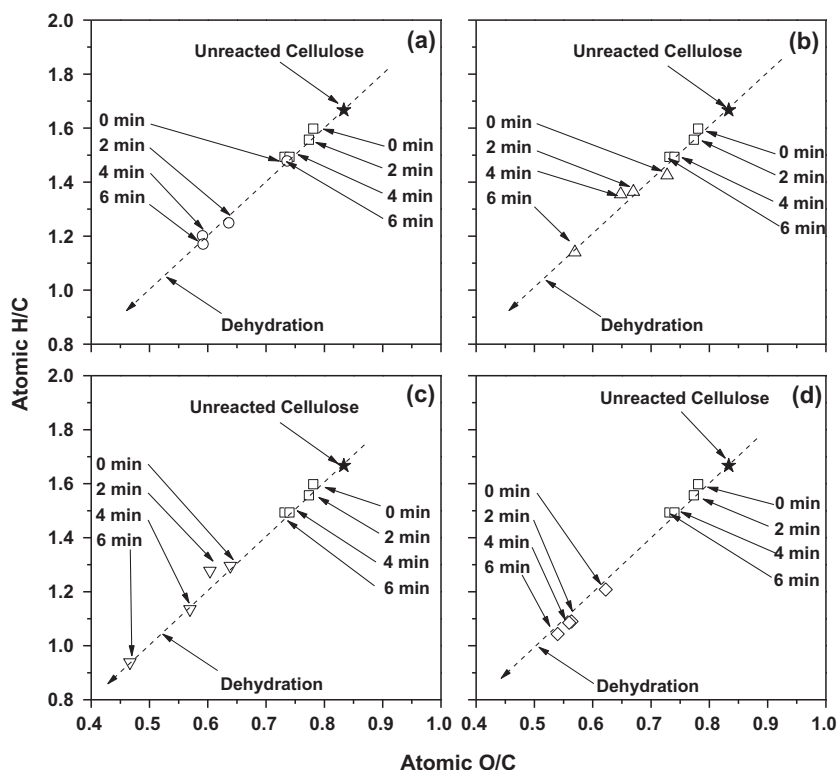

Fig. 2. Van Krevelen diagrams for the solid residues generated from the pyrolysis of raw (square) and salt-loaded celluloses at 325 °C. Panel (a) NaCl-loaded cellulose (circle); (b) KCl-loaded cellulose (triangle); (c) MgCl$_2$-loaded cellulose (inverted triangle); (d) CaCl$_2$-loaded cellulose (diamond).
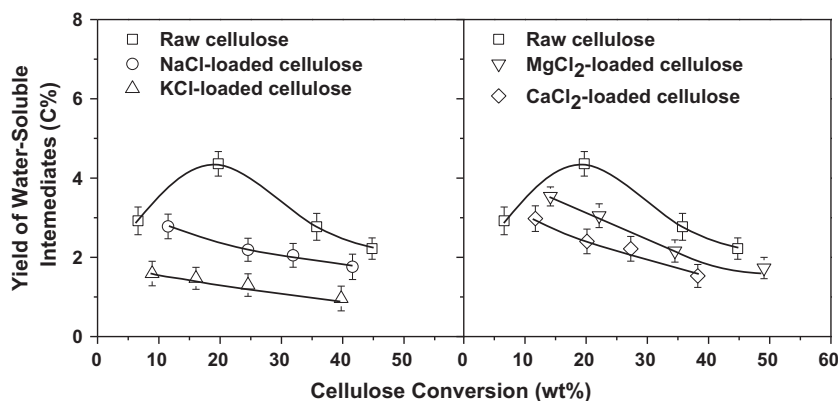
Fig. 3. A comparison of the yield of water-soluble intermediates (on a carbon base) from the fast pyrolysis of raw and salt-loaded celluloses at 325 °C.

various salt-loaded celluloses are lower than that from raw cellulose, especially at conversions higher than 10%. The data in Fig. 3 also reveals the differences in the yields of water-soluble intermediates from various salt-loaded celluloses. The yields of water-soluble intermediates from the $MgCl_2$-loaded and $CaCl_2$-loaded celluloses are higher than those from the KCl-loaded and NaCl-loaded celluloses. For example, the yield of water-soluble intermediates from the $CaCl_2$-loaded cellulose is ~3% during the heating-up period, which is higher than that from the KCl-loaded cellulose (~1.6%). According to our previous studies [22,24,25], the formation of water-soluble intermediates is mainly determined by the structures of pyrolyzing cellulose, i.e., the hydrogen bonding network and the cross-linking structures. The higher yield of water-soluble intermediates from alkaline earth metal chloride-loaded celluloses is likely due to the more effective alkaline earth metals to weaken the hydrogen bonding network in cellulose. As pyrolysis proceeds, the yields of water-soluble intermediates in all salt-loaded samples continuously reduce, because of the more cross-linked structures in pyrolyzing cellulose. The yields of water-soluble intermediates follow the order of $MgCl_2$-loaded > $CaCl_2$-loaded > NaCl-loaded > KCl-loaded cellulose. Generally, a high yield of water-soluble intermediates leads to a high weight conversion, as water-soluble intermediates are the main precursors of volatiles. For example, the $MgCl_2$-loaded cellulose yields the highest water-soluble intermediates among the salt-loaded celluloses, leading to the highest weight conversion (see Fig. 1a). However, even though the yield of water-soluble intermediates from $CaCl_2$-loaded cellulose is higher than those from the NaCl-loaded and KCl-loaded celluloses, its weigh conversion is still

the lowest among all the salt-loaded celluloses. It is known that the water-soluble intermediates not only evaporate into vapor phase as volatiles (leading to a high weigh conversion), but also re-polymerize into water-insoluble portion to form char (leading to a low weight conversion). The results in this study indicate that the water-soluble intermediates are easily re-polymerized back into water-insoluble structures for the $CaCl_2$-loaded cellulose, leading to a reduced weight conversion.

3.2.2. Sugar yields of the water-soluble and water-insoluble portions of solid residues

Post-hydrolysis was then conducted to determine the sugar contents of both water-soluble and water-insoluble portions of the solid residues during the pyrolysis of the salt-loaded celluloses, and the results are shown in Fig. 4. The addition of salts is found to promote the degradation of sugar structures in both water-soluble and water-insoluble portions. The sugar contents of the water-insoluble portion follow the order of NaCl-loaded > KCl-loaded > $MgCl_2$-loaded > $CaCl_2$-loaded cellulose. The results suggest that the sugar contents in the alkaline earth metal-loaded celluloses are much lower, which is due to the significant dehydration reactions during the heating-up period. Moreover, the loaded salts may further catalyze the degradation of sugar structures during the isothermal pyrolysis, depending on the distribution of inorganic species in the reaction intermediates.

The contents of inorganic species in the water-insoluble portion were further determined, and the results are shown in Fig. 5. The majority of the alkaline earth metals have become water-insoluble even during the heating-up period, especially for the $CaCl_2$-loaded
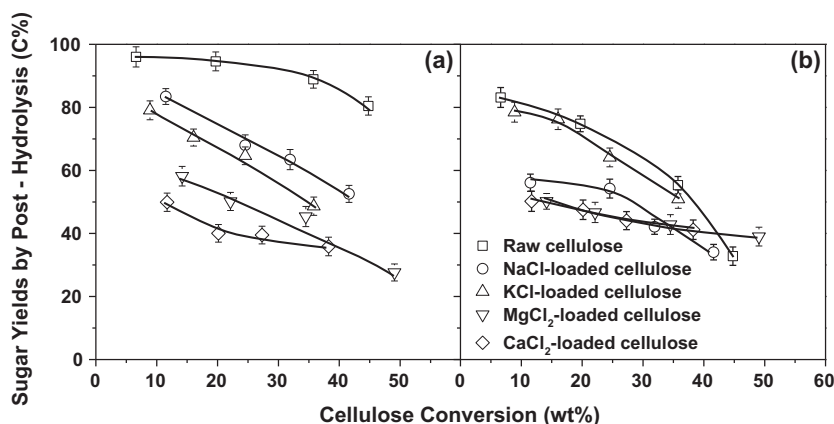

Fig. 4. Yields of hydrolysable sugar in the water-soluble and water-insoluble portions of the solid residues generated from the pyrolysis of raw and salt-loaded celluloses at 325 °C. Panel (a) water-insoluble portion; (b) water-soluble portion.
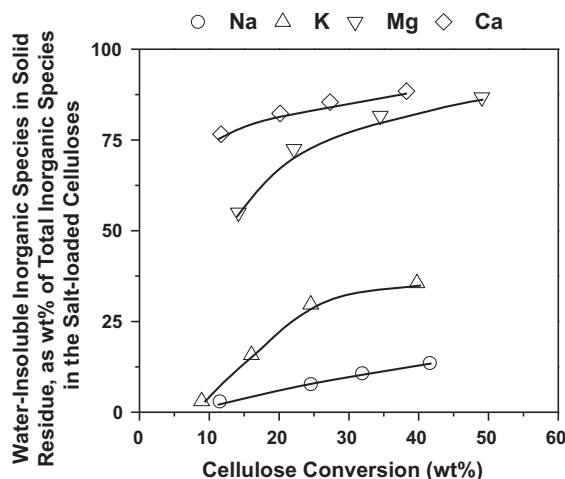
Fig. 5. The inorganic species in the water-insoluble portions (as wt% of total inorganic species in the salt-loaded celluloses) from the solid residues generated from the pyrolysis of the salt-loaded celluloses at 325 °C.

cellulose. For example, ∼76% of Ca and ∼55% of Mg become water-insoluble during the heating-up period, compared to that only ∼3% of Na and K are in the water-insoluble portion. This indicates that significant interactions take place between alkaline earth metals and cellulose structures during the pyrolysis of the alkaline earth metal chloride-loaded celluloses, while such interactions are much weaker for the alkali metal chloride-loaded celluloses. During the isothermal pyrolysis, more inorganic species become water-insoluble. For example, after holding for 6 min, ∼32% of K and ∼31% of Mg are converted into water-insoluble forms, in comparison to only ∼10% and ∼12% for Na and Ca. While the detailed chemical forms of these water-insoluble metallic species in the solid residues are unknown, these metallic species are most likely in ion-exchangeable forms. This is because that although the oxides or carbonates of Na or K are water soluble, at least some of Na or K are still water-insoluble hence these water-insoluble forms Na or K are most likely in ion-exchangeable forms in the solid residues. This is consistent with our related study on the release of Cl during the pyrolysis of the NaCl-loaded cellulose at 150–400 °C [31]. At temperatures below 350 °C, it was evident that the loaded NaCl interacts with the organic structure of cellulose so that Na is bound into the organic structure while Cl is released mainly as HCl (g) under the pyrolysis conditions [31].

The results in Fig. 4b suggest that the sugar content in water-soluble portion is also influenced by the type of salt added into cellulose. The sugar contents of the water-soluble portion are lower for the alkaline earth metal chloride-loaded celluloses. This is reasonable since the water-soluble portion is generated from the water-insoluble portion, which is largely contributed by non-sugar structures for the alkaline earth metal chloride-loaded celluloses. Also, the sugar yields of the water-soluble portion in the alkali metal chloride-loaded celluloses reduce much more significantly than those of the alkaline earth metal chloride-loaded celluloses, probably due to the strong catalytic effect of inorganic species as the majority of alkali metals are in the water-soluble forms.

3.2.3. Distributions of sugar and non-sugar structures in solid residues

Based on the above data, the distribution of sugar and non-sugar structures in the water-soluble and water-insoluble portions of solid residues can be calculated, and the data are shown in Fig. 6. The yields of sugar and non-sugar structures in the water-soluble portion are small, obviously due to the low yield of water-soluble intermediates.
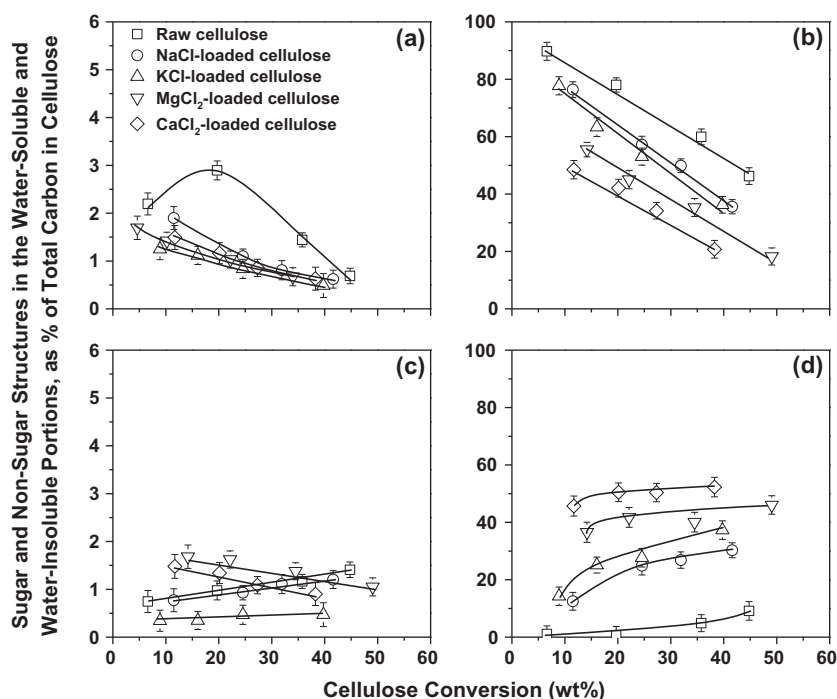
For the sugar structures in the water-insoluble portion, around half of the sugar structures are decomposed during the heating-up period for the MgCl$_2$-loaded and CaCl$_2$-loaded celluloses, compared to around 22% for the NaCl-loaded and KCl-loaded celluloses. During the isothermal pyrolysis, the sugar structures in the water-insoluble portions continue to reduce as pyrolysis proceeds (see Fig. 6b). After holding for 6 min, the yields of sugar structures reduce by ∼42%, ∼39%, ∼39% and ∼25% for the NaCl-loaded, KCl-loaded, MgCl$_2$-loaded and CaCl$_2$-loaded celluloses, respectively, which corresponds to a sugar conversion of ∼54%, ∼52%, ∼68% and ∼51% if based on the sugar structures at zero holding time. Considering the majority of Mg and Ca are in the water-insoluble forms, it is likely that the decomposition of sugar structures in the water-insoluble portion is not significantly affected by the water-insoluble inorganic species which are most likely bonded with non-sugar structures [30].

For the non-sugar structures in the water-insoluble portion, majority of non-sugar structures are produced during the heating-up period for the MgCl$_2$-loaded and CaCl$_2$-loaded celluloses, while the formation of non-sugar structures during the isothermal pyrolysis is small. For example, the yields of non-sugar structures only increase by ∼10% and ∼7% during the isothermal pyrolysis for the MgCl$_2$-loaded and CaCl$_2$-loaded celluloses, respectively. In comparison to the alkaline earth metal chloride-loaded celluloses, even though the alkali metal chloride-loaded celluloses produce much less non-sugar structures during the heating-up period, a substantial increase in the yield of non-sugar structures can be found during the subsequent isothermal pyrolysis. For example, the yields of non-sugar structures increase by ∼18% and ∼23% for the NaCl-loaded and KCl-loaded celluloses, respectively. Additionally, the water-insoluble inorganic species seem to have less effect on the formation of non-sugar structures in the water-insoluble portion, as a significant amount of the water-insoluble Mg and Ca does not lead to a significant increase in the yield of non-sugar structures in the water-insoluble portion during the subsequent isothermal pyrolysis. In contrast, substantial non-sugar structures are produced in the water-insoluble portion during the isothermal pyrolysis of the NaCl-loaded and KCl-loaded celluloses. This is more likely due to the catalytic effect of mobile (unbonded) inorganic species to convert sugar structures into non-sugar structures (i.e., by dehydration), since majority of Na and K are still in the water-soluble forms.
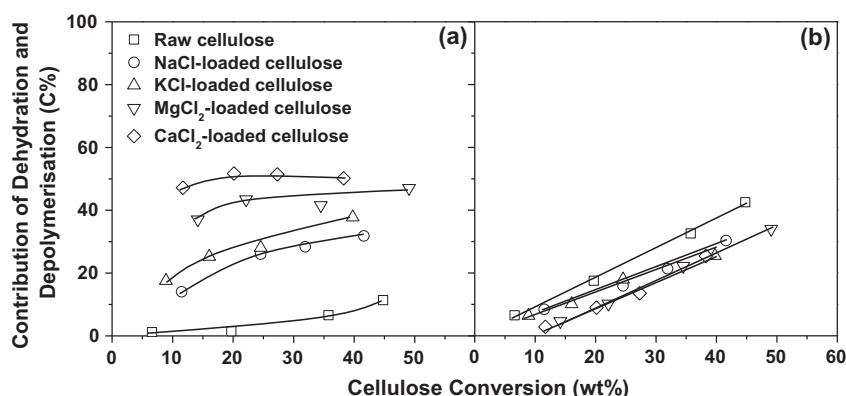
3.3. Contribution of depolymerization and dehydration reactions during the pyrolysis of various salt-loaded celluloses

The sugar conversion during cellulose pyrolysis is mainly due to the depolymerization and dehydration reactions at low temperatures [15]. Based on the above data, the contribution of depolymerization and dehydration reactions to sugar conversion during the pyrolysis of various salt-loaded celluloses can be further compared. Since the carbon conversion (see Fig. 1) is mainly caused by depolymerization reactions and the sugar conversion is due to both dehydration and depolymerization reactions [15], Fig. 7 illustrates the contribution of two reactions to sugar conversion at various conversion levels, and several important findings can be observed. First, the addition of salt significantly promotes the dehydration reactions during the heating-up period (see Fig. 7a), due to the weakening of hydrogen bonding networks by added salts. The promotion of dehydration reactions for various salts during the heating-up period follows the order of CaCl$_2$ > MgCl$_2$ > KCl > NaCl. However, the contribution of dehydration reactions to sugar conversion increases slowly during the isothermal pyrolysis for the CaCl$_2$-loaded and MgCl$_2$-loaded celluloses. For example, the sugar conversion due to dehydration during isothermal pyrolysis at 325 °C for 6 min only increases by ∼3% and ∼10% for the

Fig. 6. Sugar and non-sugar structures (as % of total carbon in cellulose) in the water-soluble and water-insoluble portions of solid residues generated from the pyrolysis of the raw and salt-loaded celluloses at 325 °C. Panel (a) sugar in water-soluble portion; (b) sugar in water-insoluble portion; (c) non-sugar in water-soluble portion; (d) non-sugar in water-insoluble portion.

Fig. 7. Contribution of depolymerization and dehydration to sugar conversion during the pyrolysis of raw and salt-loaded celluloses at 325 °C. Panel (a) sugar conversion due to dehydration reactions; (b) sugar conversion due to depolymerization reactions.

$CaCl_2$-loaded and $MgCl_2$-loaded celluloses, respectively, while those for the NaCl-loaded and KCl-loaded celluloses increase by ~17% and ~20%, respectively. However, based on the data in Fig. 1, the water yield (calculated based on weight and carbon conversions) still continuously increases during the isothermal pyrolysis for the $CaCl_2$-loaded and $MgCl_2$-loaded celluloses. For example, during the isothermal pyrolysis at 325 °C for 6 min, the yield of water increases from ~10% to ~15% for the $MgCl_2$-loaded cellulose, and from ~9% to ~13% for the $CaCl_2$-loaded cellulose. Therefore, significant dehydration reactions still occur, but mainly from the non-sugar structures as such dehydration reactions do not lead to a significant increase in sugar conversion. Since ~77% of Ca and ~55% of Mg have become water-insoluble during the heating-up period (see Fig. 5), it is reasonable that the majority of dehydration reactions occur in the non-sugar structures as the inorganic species are already bonded with non-sugar structures during the

isothermal pyrolysis for the $CaCl_2$-loaded and $MgCl_2$-loaded celluloses. In contrast, dehydration reactions still play an important role in the sugar conversion during the isothermal pyrolysis of the NaCl-loaded and KCl-loaded celluloses, as the majority of Na and K are still in the water-soluble forms during the isothermal pyrolysis (see Fig. 5).

Second, in comparison to dehydration reactions, significant depolymerization reactions take place during the isothermal pyrolysis for all salt-loaded celluloses. For example, the sugar conversion due to depolymerization reactions during the heating-up period is only ~8%, ~6%, ~5% and ~3% for the NaCl-loaded, KCl-loaded, $MgCl_2$-loaded and $CaCl_2$-loaded celluloses, respectively. However, during the isothermal pyrolysis for 6 min, the sugar conversion due to depolymerization reactions increases by ~24%, ~19%, ~29% and ~23%, respectively. Such results indicate that the loaded salts seem to have less influence on the depolymeriza-

tion reactions during the isothermal pyrolysis. It is noteworthy that the sugar conversions due to depolymerization reactions for the salt-loaded celluloses are considerably lower than that (~36%) for the raw cellulose. This main reason is that the amount of sugar structures reduces substantially during the heating-up period for the salt-loaded celluloses. Based on the amount of sugar structures at zero holding time, the sugar conversion due to depolymerization is ~39%, ~31%, ~25%, ~50%, ~45% for the raw, NaCl-loaded, KCl-loaded, $MgCl_2$-loaded and $CaCl_2$-loaded celluloses, respectively. Therefore, the depolymerization reactions are enhanced during the isothermal pyrolysis for the $MgCl_2$-loaded and $CaCl_2$-loaded celluloses, but are suppressed for the NaCl-loaded and KCl-loaded celluloses.

Third, for the pyrolysis of the alkali metal chloride-loaded celluloses, dehydration reactions play a major role in sugar conversion during the heating-up period, whereas depolymerization reactions play a minor role. However, the depolymerization reactions become more important during the isothermal conversion. For example, during the pyrolysis of the NaCl-loaded cellulose, the dehydration and depolymerization reactions contribute to ~62% and ~38% of sugar conversion (leading to a ~22% sugar conversion) during the heating-up period, and contribute to ~43% and ~57% of sugar conversion (leading to a ~42% sugar conversion) during the isothermal conversion at 325 °C for 6 min. The promotion of KCl to dehydration reaction is slightly stronger. For example, during the pyrolysis of the KCl-loaded cellulose, the dehydration and depolymerization reactions contribute to ~73% and ~27% of sugar conversion (leading to a ~24% sugar conversion) during the heating-up period, and contribute to ~51% and ~49% of sugar conversion (leading to a ~39% sugar conversion) during the isothermal conversion at 325 °C for 6 min.

However, for the pyrolysis of alkaline earth metal chloride-loaded celluloses, dehydration reactions plays a dominant role in sugar conversion during the heating-up period, whereas depolymerization reactions play a dominant role in sugar conversion during the isothermal pyrolysis. For example, during the pyrolysis of the $MgCl_2$-loaded cellulose, the dehydration and depolymerization reactions contribute to ~89% and ~11% of sugar conversion (leading to a ~42% sugar conversion) during the heating-up period, and contribute to ~25% and ~75% of sugar conversion (leading to a ~39% sugar conversion) during the isothermal conversion at 325 °C for 6 min. Such a phenomenon is more obvious for the $CaCl_2$-loaded cellulose. For example, during the pyrolysis of the $CaCl_2$-loaded cellulose, the dehydration and depolymerization reactions contribute to ~94% and ~6% of sugar conversion (leading to a ~50% sugar conversion) during the heating-up period, and contribute to ~12% and ~88% of sugar conversion (leading to a ~26% sugar conversion) during the isothermal conversion at 325 °C for 6 min.

Such different effects of alkali and alkaline earth metal chlorides are mainly due to the transformation of inorganic species as different forms during cellulose pyrolysis. For alkali metals, a majority of them are in the water-soluble forms, so it is easy for alkali metals to catalyze the dehydration reactions during both the heating-up period and the isothermal pyrolysis period. For alkaline earth metals, a majority of them are transformed into the water-insoluble forms after the heating-up period, thus reducing their catalytic effects on the dehydration of sugar structures during the isothermal pyrolysis period. Rather, the water-insoluble forms play an important role in the dehydration of non-sugar structures during the isothermal pyrolysis.

4. Conclusions

This work compares the evolution of solid residues from various salt-loaded celluloses during fast pyrolysis at 325 °C. As stronger Lewis acids, the alkaline earth metal ions (Mg^{2+} and Ca^{2+}) are more effective than the alkali metal ions (Na^+ and K^+) to catalyze the dehydration reactions of sugar structures even during the heating-up stage, producing a more cross-linked cellulose for the subsequent isothermal pyrolysis. As a result, the majority of Mg and Ca are transformed into water-insoluble forms during the heating-up stage, suppressing the dehydration of sugar structures but enhancing the dehydration of non-sugar structures during the isothermal pyrolysis. In contrast, the enhancement on the dehydration of sugar structures during the heating-up stage is less significant for the alkali metal chlorides such as NaCl and KCl. After the heating-up stage, the majority of Na and K are water-soluble and able to further catalyze the dehydration reactions of sugar structures during the isothermal pyrolysis. Compared to dehydration reactions, depolymerization reactions are less influenced by the loaded salts, resulting in a significant contribution to sugar conversion during the isothermal pyrolysis.

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